from the side away from the solution carrier, so that the organic solvent solutions used (especially those containing oxidant-sensitive pyridinyl radicals) have an absolute minimum of contact with the glue. (C) Carriage mechanism: (1) threaded sleeve and (2) micrometer drum fixed to the inner cylinder by a stainless steel insert. (D) Structural support: (1) aluminum barrel around the outer cylinder and (2) stainless steel pin to halt motion of inner barrel. (E) External connection: a side arm is sealed to the outer cylinder and connects the cell to the vacuum line or another tube carrying an oxygen-free solution.

The dimensions of the cell are indicated in the caption to Figure 9. Mounted on an appropriate base, the cell may be placed in the Cary Model 17 spectrophotometer cell compartment. The sapphire windows permit IR spectra to be measured to wavelengths as long as 6200 nm.

The path length in the VV-cell may be varied from 0.001 to 0.8 cm (paths as long as 5–10 cm might be considered). Cell solution volume, including the external tube, may be 1–30 mL. A calibrated pipet is used as a second arm. Dilutions can be carried out by placing a solution of known concentration in the cell and distilling solvent from the calibrated pipet until the volume in the pipet has fallen to the desired level. More conveniently, a dilute solution in the cell is concentrated by distilling solvent from the cell and measuring the volume increase in the pipet. Temperature equilibration of the apparatus is necessary for accurate volume measurement. The temperature coefficient of expansion for CH_3CN is particularly high. Mixing after the removal or addition of solvent is carried out by pouring the solution back and forth at right angles to the direction in which the cell is connected to the calibrated pipet.

Spectra can be measured over a concentration range of about 1000 with the apparatus, as we showed with a study of the concentration variation of the 395-nm absorption band shape of 1-*tert*-butyl-4-(carbomethoxy)pyridinyl radical. In order to simplify the comparison of the spectra, the absorption maxima were matched in height for all concentrations, a task that would have been quite difficult without the VV-cell.

Polarographic Measurements. Reduction potentials were obtained with a two-electrode system, measuring and controlling potentials with a linear scan generator (Model S6-5, Specific Electronic, Ltd.), using a current-to-voltage converter for current measurement[21] and an X-Y re-

corder. The counter electrode served as reference electrode (Ag/AgNO$_3$ (0.01 M), LiClO$_4$ (0.4 M)/CH$_3$CN). Anolyte was separated from catholyte (LiClO$_4$, 0.4 M; depolarizer, 10^{-4}–10^{-3} M) by a porous glass tube (Corning 7930 glass) and was changed every day. Measurement of a Radiometer K-401 SCE electrode in the system yielded a value of about 0.22 V, a number which may be added to obtain the potentials vs. the SCE reference electrode.

The reduction potentials were verified with 1-methyl-4-carbamido-pyridinium ion, which gave a potential of –1.156 V for the two-electrode system used here and –1.154 v for a three-electrode system measurement.[22]

Preparation of Pyridinium Salts. The 1-*tert*-Butylpyridinium salts were prepared from the 1-(2,4-dinitrophenylpyridinium) derivative and *tert*-butylamine.[23] The 1-isopropyl-4-(carbo-*tert*-butoxy)pyridinium salts were prepared by the same route, using isopropylamine. Details have been given elsewhere.[4] The 1-alkyl-4-carbamidopyridinium iodides were prepared from the corresponding 4-(carbomethoxy)pyridinium derivatives by treatment with NH$_3$/CH$_3$OH, the iodide salts being precipitated by the addition of ether followed by recrystallization from methanol/ether. The properties of the salts are as follows. 1-*tert*-Butyl-4-(carbo-*tert*-butoxy)pyridinium iodide: mp 200–202 °C, *p*-toluenesulfonate, mp 159–160 °C; ^{1}H NMR (D$_2$O) 1.84 (s, 9 H), 2.07 (s, 9 H), 8.79 (br, 2 H), 9.54 (br, 2 H) ppm; UV (CH$_3$CN) [λ_{max} (ϵ_{max})] 273 nm (4700), I$^-$ peak at 246 nm.[24] 1-*tert*-Butyl-4-carbamidopyridinium iodide: mp 222–223 °C; 1H NMR (D$_2$O) 1.81 (s, 9 H), 8.34 (d, J = 11 Hz, 2 H), 9.00 (d, J = 11 Hz, 2 H) ppm. 1-Isopropyl-4-(carbo-*tert*-butoxy)-pyridinium iodide: 220–230 °C dec, *p*-toluenesulfonate, mp 133–134 °C. All other pyridinium salts have been described in previous papers.[2,4]

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Stable Free Radicals. 13. A Reinvestigation of the Pyridinyl Diradical, 1,1'-Trimethylenebis(4-(carbomethoxy)pyridinyl)[1]

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Abstract: The absorption spectrum attributed to 1,1-trimethylenebis(4-(carbomethoxy)pyridinyl) (3··) includes major contributions from intramolecularly cyclized forms, "cyclomers": *cis*-A-3 and *trans*-3. The broad, temperature-sensitive, and medium-sensitive absorption bands of the cis A and trans cyclomers arise from $\pi-\sigma \rightarrow \pi-\sigma^*$ transitions. The 3 cyclomers are transformed into diradical metal ion complexes, 3··M^{n+}, by MClO$_4$, and the cyclomers are reformed by removal of the metal ion with donors. Diradical oxidation level species belong to the ⟨3⟩ system. The components are in equilibrium with one another and can be converted into the ⟨3⟩M^{n+} complexes. Reduction of the bispyridinium ion 3^{2+} with Na(Hg) leads mainly to the trans cyclomer; electrochemical reduction in the presence of LiClO$_4$ or Mg(ClO$_4$)$_2$ yields the diradical complexes, 3··M^{n+}, but with *n*-Bu$_4$NClO$_4$ it yields the trans cyclomer. An initial preponderance of another cyclomer, *cis*-B-3, is replaced by *trans*-3 ($t_{1/2}$, 1 s). Isopentane extraction of *trans*-3 yields a variable (usually 1:2) mixture of *cis*-A-3 and *trans*-3. The spectrum of a thin film of distilled ⟨3⟩ resembles that of the isopentane extract. Partial reduction of 3^{2+}, either with 1-methyl-4-(carbomethoxy)pyridinyl (4·) or electrochemically, gives the radical cation 3$^+$·, which exhibits an intervalence transition at 1360 nm. The disproportionation constant, $K = [3^+\cdot]^2/[3^{2+}][3\cdot\cdot] = \sim 0$–18, depends on medium, with low values found when 3··Mg^{2+} is present. The previously reported spectrum of 3$^+$· must include a contribution from *trans*-3. A complete scheme is given which includes 3^{2+}, 3$^+$·, and various ⟨3⟩ species: cyclomers, open diradicals, and diradical metal ion complexes.

The discovery of stable pyridinyl radicals (4·)[1,3] was soon followed by the report of diradicals in which two to five methylene

groups separated the 4-(carbomethoxy)pyridinyl moieties.[4,5] Later studies revealed that pyridinyl diradical metal ion complexes had

spectra significantly different from those of the diradicals,[1c] but the differences were attributed to the influence of the metal ions.

After we discovered (a) that **4·** radicals could form covalent dimers in thin films,[1e] (b) that the long wavelength absorption could be explained by a $\pi\text{-}\sigma \rightarrow \pi\text{-}\sigma^*$ transition, and (c) that metal ion could stabilize 4-(carbomethoxy)pyridinyl radicals, we undertook a reinvestigation of the pyridinyl diradical **3··** and radical cation **3⁺·**[6] and report the results in the present article.

Results

Reduction with Pyridinyl Radicals. The stable pyridinyl radical **4·** was used to reduce 1,1′-trimethylenebis(4-(carbomethoxy)-pyridinium) diiodide ($3^{2+}2I^-$) to avoid metal ions and to check our previous report.[7] Weighed amounts of $3^{2+}2I^-$ were added
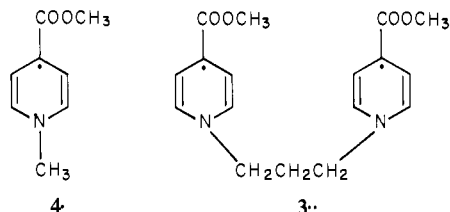
to solutions of **4·** in CH_3CN, with reaction followed by UV, vis, and near-IR spectra, as illustrated in Figure 1. The first addition sharply diminished the pyridinyl radical absorption at 395 (6500) and 305 (13 500),[8] the solution exhibiting a maximum at 392 (2000) and shoulders at 440 (400), 305 (4000), and 275 (7000). Another addition of $3^{2+}2I^-$ (bis-cation/radical now 1:1) gives rise to a maximum at 381 (3500), an increase in the shoulder at 440 (530), and a new absorption band in the near-IR at 1360 (1000). (The expected py^+I^- charge-transfer absorption band[9] near 400 nm has an ϵ value of about 100.) Further additions of $3^{2+}\text{-}2I^-$ increase the band intensities: 305 (8500), 381 (6700), 440 (sh, 2000), and 1360 (1650).

Electrochemical Reduction (Bu_4NClO_4). Quantitative electrochemical reduction of $3^{2+}2ClO_4^-$ (0.099 mM) in CH_3CN–Bu_4NClO_4 (67 mM) was carried out with the spectroelectrochemical cell previously described.[1d] After passage of 0.76 e/mol of 3^{2+}, the solution showed maxima at 381 (3700), 275 (10 000) [3^{2+}: λ_{max} 275 (9300)], and 1360 (900) (not shown) with shoulders at 240, 275, 302, and 440. Further reduction (1.52 e⁻/mol of 3^{2+}) led to various changes in each band and another absorption at 600 (200). Finally, after 2.28 e⁻/mol of 3^{2+}, the spectrum had a broad band at 400 (3000), a shoulder at 440 (1900), and no bands at 275 and 1360. The spectra are shown in Figure 2.

Electrochemical Reduction ($LiClO_4$, $Mg(ClO_4)_2$). Reduction of $3^{2+}2ClO_4^-$ in CH_3CN–$LiClO_4$ (270 mM) leads to strong pyridinyl radical bands (305, 377 nm) accompanied by a strong visible π-mer absorption (605 nm) (Figure 3). The solution does not show appreciable absorption at 1360 nm ($\epsilon < 100$) after partial
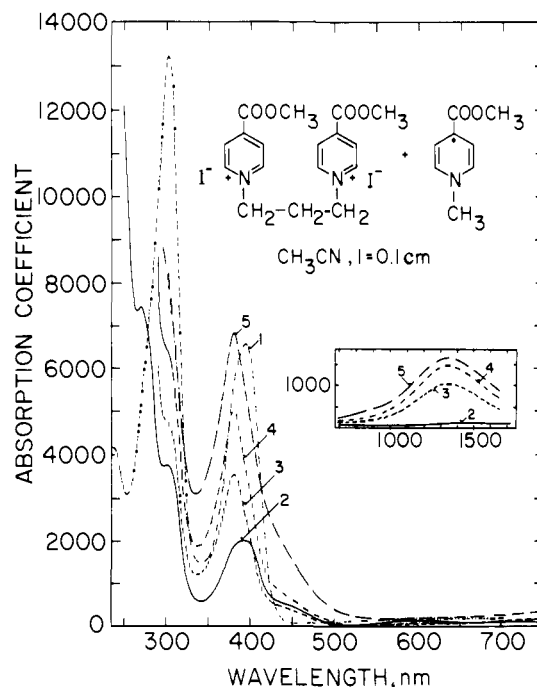

Figure 1. Spectra for successive additions of 1,1′-trimethylenebis(4-(carbomethoxy)pyridinium) diiodide ($3^{2+}2I^-$) to 1-methyl-4-(carbomethoxy)pyridinyl (**4·**) in CH_3CN. Curve 1 (-----): **4·** (1.66 mM) with maxima at 395 (6500) and 305 nm (13 500). Curve 2 (–): after addition of $3^{2+}2I^-$ (0.6 mM), much **4·** absorption is lost, with a maximum at 392 nm (2000) and shoulders at 440 (400), 305 (4000), and 275 nm (7000). Curve 3 (- -): after addition of $3^{2+}2I^-$ (1.61 nM), UV maximum at 381 nm (3500), new maximum at 1360 nm (1000). Curve 4 (···): after addition of $3^{2+}2I^-$ (3.23 mM). Curve 5 (—): after addition of $3^{2+}2I^-$, final maxima at 381 (6700) and 1360 nm (1650), with shoulders at 305 (8500) and 440 nm (2000). The inset illustrates the near-IR spectrum between 700 and 1700 nm.
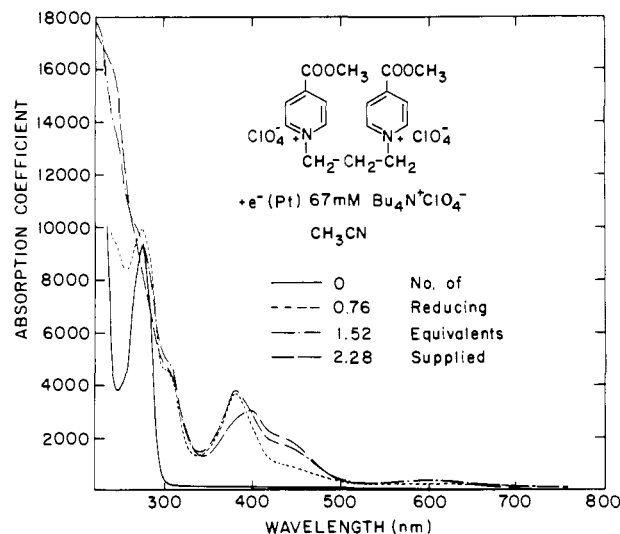

Figure 2. Spectra for electrochemical reduction of $3^{2+}2ClO_4^-$ (0.099 mM) in CH_3CN–Bu_4NClO_4 (67 mM). Curve 1 (—): before reduction, maximum at 275 nm (9300). Curve 2 (- -): after passage of 0.76 e⁻/mol of bis-cation, maxima at 381 (7100), 275 (10 000), and 1360 nm (900), near-IR not shown. Curve 3 (···): after passage of 1.52 e⁻/mol of bis-cation, loss of 275 nm, gain of 440 nm (1900). Curve 4 (– –): after passage of 2.28 e⁻/mol of bis-cation, maximum at 400 nm (3000), shoulder at 440 nm (2100), no 381- or 1360-nm bands.

(1) Previous articles in this series include (a) Kosower, E. M.; Waits, H. P.; Teuerstein, A.; Butler, L. C. *J. Org. Chem.* **1978**, *43*, 800–805; (b) Kosower, E. M.; Teuerstein, A. *J. Am. Chem. Soc.* **1978**, *100*, 1182–1185; (c) Kosower, E. M.; Hajdu, J.; Nagy, J. H. *Ibid.* **1978**, *100*, 1186–1193; (d) Hermolin, J.; Levin, M.; Ikegami, Y.; Sawayanagi, M.; Kosower, E. M. *Ibid.*, accompanying paper in this issue. (e) Hermolin, J.; Levin, M.; Kosower, E. M. *Ibid.*, accompanying paper in this issue. (f) Hermolin, J.; Levin, M.; Kosower, E. M. *Ibid.*, accompanying paper in this issue. (g) Hermolin, J.; Kirowa-Eisner, E.; Kosower, E. M., *Ibid.* **1981**, *103*, 1591–1593.

(2) (a) Tel-Aviv University; (b) State Univesity of New York, Stony Brook.

(3) Summarized in Kosower, E. M. In "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. 1, Chapter 1; Kosower, E. M. *ACS Symp. Ser.* **1978**, *69*, 447–456.

(4) Kosower, E. M.; Ikegami, Y. *J. Am. Chem. Soc.* **1967**, *89*, 461–462.

(5) Itoh, M.; Kosower, E. M. *J. Am. Chem. Soc.* **1968**, *89*, 1843–1849.

(6) Itoh, M. *J. Am. Chem. Soc.* **1971**, *93*, 4750–4754.

(7) Kosower, E. M.; Teuerstein, A. *J. Am. Chem. Soc.* **1976**, *98*, 1586–1587.

(8) The absorption coefficients are appreciably higher than those previously reported as a result of a revision in the absorption coefficient for the reference material, 1,1′-dimethyl-4,4′-bipyridylium cation radical ($PQ^+\cdot$) and some improvements in technique which led to purer solutions of radicals like **4·** (see ref 1d).

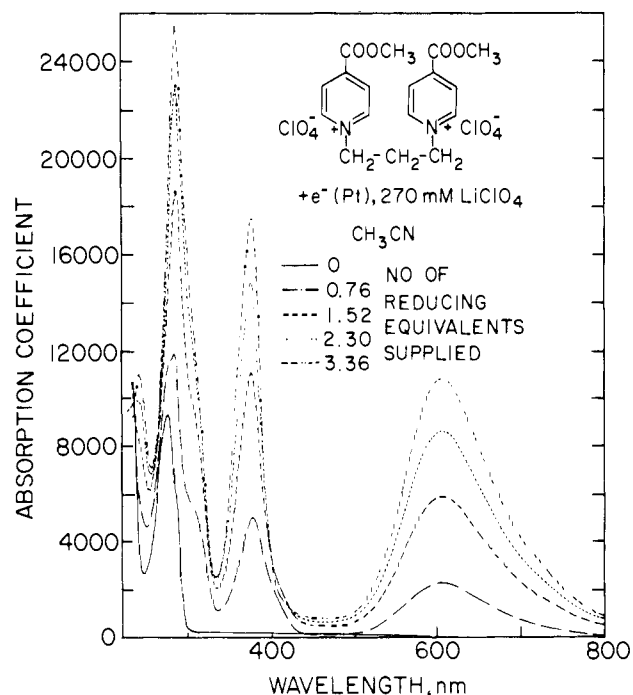(9) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253–3260.

reduction. Even small amounts of $LiClO_4$ (3.1 or 23 mM) change the course of the reduction but still lead to 75% or 50%, respectively, of the 1360-nm intensity noted without the salt. Reduction in the presence of Bu_4NClO_4 (72 mM) and $Mg(ClO_4)_2\cdot3H_2O$ (3 mM) gave results similar to those found for 270 mM $LiClO_4$.

Figure 3. Spectra for electrochemical reduction of $3^{2+}2ClO_4^-$ (0.094 mM) in CH_3CN–$LiClO_4$ (270 mM). The contrast with the spectra shown in Figure 2 is striking. Passage of 0 (–), 0.76 (–··–), 1.52 (- - -), 2.30 (···), and 3.36 (–····–) e^-/mol of bis-cation lead to successive increases in visible absorption at 605 nm and in the pyridinyl radical bands at 377 and 305 nm. No absorption at 1360 nm is seen at any stage of the reduction.

Sodium Amalgam Reduction. The reaction of $3^{2+}2I^-$ with $Na(Hg)/CH_3CN$[10] leads first to solutions containing 3^+· (25% according to 1360-nm absorption intensity) and a broad absorption near 400 nm, with final solutions containing mainly the latter. Addition of *t*-Bu, $4^+ClO_4^-$ yields the corresponding 4· (not illustrated).

Distillation of 3··. Reduction of $3^{2+}2Br^-$ with Na(Hg) in CH_3CN to the final stage just described, removal of the solvent, and extraction with isopentane gave a solution of "diradical 3··" with a spectrum similar to that previously reported.[6] Since Ikegami[11] has noted that sodium iodide was present in an isopentane extract of 2··,[4] the diradical 3·· was "plated" on the sapphire window of the thin-film spectroscopy apparatus[1c] by distillation in high vacuum. The spectrum of the thin film was very similar to that of the initial CH_3CN solution, with two broad bands observed at 400 (3000) and 730 nm (3000). Neither annealing nor irradiation of the film led to any significant changes in spectrum.

Discussion

Our previous reports on pyridinyl diradicals[4,5] (py·$(CH_2)_n$Py·) revealed 2e reduction (titration) and pyridinyl radical-like spectra, properties which seemed compatible only with their formulation as diradicals. The weak EPR spectrum (1–2% of the intensity expected for 3··) was attributed to the predominance of a face-to-face ("closed") form in the singlet diradical state. Recent discoveries about the dimerization of stable pyridinyl radicals and the spectrum of the dimers have now allowed us to recognize the "closed" form as a mixture of several covalently bonded intramolecular dimers, called *cyclomers*.

The 2· pyridinyl radicals are primarily in the dimeric form (2-2) in both solution and thin films.[1d] The 4· radicals dimerize to 4-4 only in thin films over a narrow and unusual temperature range, from –100 to –20 °C.[1f] The long wavelength and broad absorption of the dimers is due to a π–$\sigma \rightarrow \pi$–σ^* transition. Both 2-2 and 4-4 dimers dissociate thermally or on irradiation and thus behave chemically as if they were radicals.
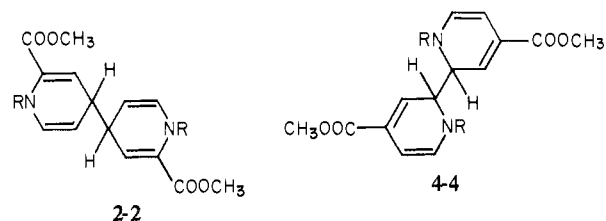
Since the diradical metal complexes, $3··M^{n+}$, have spectra that are very similar to those of simple pyridinyl radicals, we conclude that diradical formation does not substantially change the electronic transitions of a pyridinyl radical, except for an extremely intense π-mer band. The $3··MgI_2$ complex does not exhibit a readily detectable EPR spectrum.[1c] The spectra found for the "diradical" in the absence of the metal ion must then represent those of covalent forms, or "cyclomers" (intramolecular dimers). The similarity in positron of the cyclomer and diradical absorptions is understandable if the cyclomer absorptions are due to π–$\sigma \rightarrow$ π–σ^* transitions. The ratio of the 400-nm to 700-nm cyclomer absorptions is quite variable, ranging from cases in which intensity at 400 nm is less than that at 700 nm to those in which only the 400-nm absorption is present. We infer that these absorptions arise from two different species, one which absorbs near 400 nm and another which absorbs at 700 nm. A third cyclomer, with a half-life of about 1 s, has been detected by electrochemical techniques.[12] The 3 cyclomers, such as the Mg^{2+} complex cited above, show a very weak EPR spectrum.[5] Either the spectrum is broadened or the diradical is in a singlet state. The species contributing to the behavior of 3·· diradicals are collectively called the ⟨3⟩ system; these together with the metal complexes are shown in Figure 4.

The structures of the species responsible for the cyclomer absorptions are assigned on the basis of probable stability and expected spectrum. The cis cyclomer A is expected to be less stable than the trans cyclomer and perhaps to absorb light in a way similar to that of a π-mer (the face-to-face π complex of pyridinyl radicals). The cis cyclomer A is thus the structure of the species responsible for the 700-nm absorption. The trans cyclomer is the structure of the species which absorbs at 400 nm. The third isomer, cis cyclomer B, is expected to have a less favorable orientation of the π systems than cis cyclomer A, with respect for the π–$\sigma \rightarrow \pi \rightarrow \sigma$ transition. Isomer B is thought to be the unstable species detected electrochemically; the last is not the open diradical since no pyridinyl radical absorption appears near the electrode during the pulse experiments.

With this background, we are now able to summarize the results of the various reduction experiments. Reduction with various agents (Na(Hg), the 4· radical, or electrochemical reduction with Bu_4NClO_4 as electrolyte) leads to the trans cyclomer, *trans*-3. Pyridinyl radicals are stabilized through interaction with Li^+ or Mg^{2+}, and the diradical complexes are, in addition, bridged by the metal ion (on the basis of the stoichiometry, diradical/metal ion, of 1:1). Addition of metal ions to solutions of 3, or reduction in the presence of Li^+ or Mg^{2+}, leads to the diradical metal ion complexes. Extraction or distillation yields a mixture of cis cyclomer A (*cis*-A-3) and trans cyclomer (*trans*-3).

The association constant for the Mg^{2+} complex of 3·· can be estimated as 1000 M^{-1} by a comparison of the absorption coefficients of solutions made chemically (one Mg^{2+} ion per diradical[1c]) and those made electrochemically with excess Mg^{2+}. The association constant for Li^+ and 3·· is 50 M^{-1}. The concentration dependence of complexation (described elsewhere[12]) shows that only one Li^+ complexes with each diradical. Since the Li^+ complex has a spectrum similar to that of the Mg^{2+} complex and since the metal ion complexes have absorption coefficients in the UV that are almost exactly twice those of the pyridinyl radical itself, the complexes are symmetrical. Thus, both Li^+ and Mg^{2+} are bridged.

(10) Kosower, E. M., Waits, H. P. *Org. Prep. Proced. Int.* **1971**, *3*, 261–267.

(11) Ikegami, Y., personal communication.

(12) Hermolin, J.; Kashti-Kaplan, S.; Kirowa-Eisner, E. *J. Electroanal. Chem.* **1981**, in press.
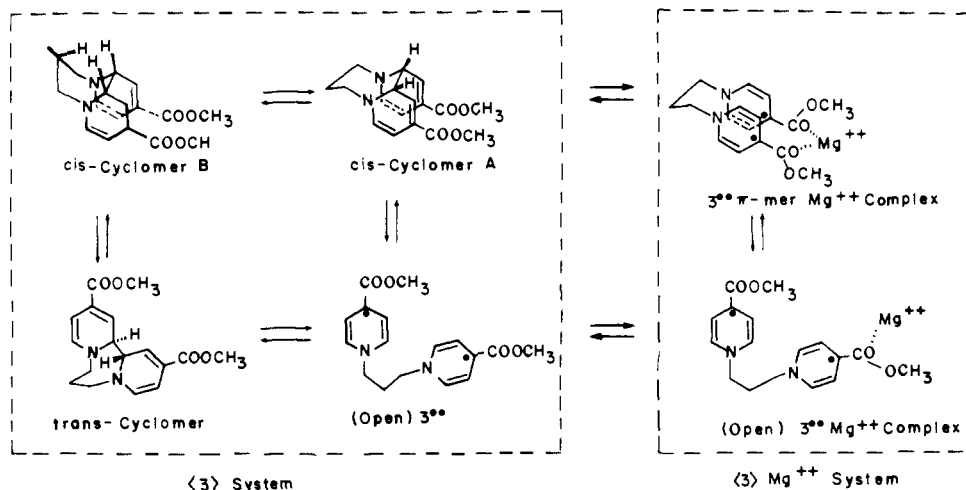
Figure 4. A scheme illustating the species that are components of the ⟨3⟩ and ⟨3⟩M^{n+} systems.

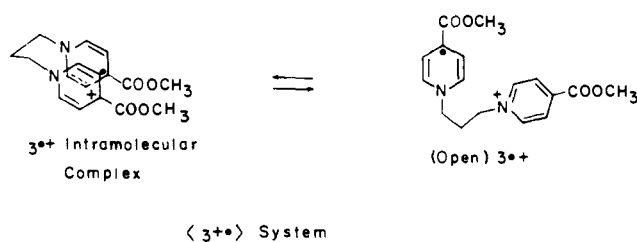**Figure 5.** The ⟨3^{+}·⟩ system, including the intramolecularly complexed species that exhibits an intervalence transition.

Transfer of the metal ion complexes from CH$_3$CN to solvents with stronger donor properties (such as pyridine) results in the conversion of the complexes to the cyclomers (see Figure 4, ref 1c).

Pyridinyl Radical Cation (3^{+}·). Partial reduction of 3^{2+}, by either chemical or electrochemical means, leads to the cation radical 3^{+}·, with maxima at 381 (6300), 305 (9000), and 1360 nm (1700). The near-IR absorption is an intervalence transition within the cation radical. The ⟨3^{+}·⟩ system, which includes the open and closed forms of the cation radical, is shown in Figure 5. The disproportionation constant for 3^{+}· can be determined from the experiment in which 3^{2+} is added to 4·, with the aid of the following equations:

$$[3^{2+}] + [3^{+}\cdot] + [\langle 3 \rangle] = [3^{2+}]_0 \qquad (1)$$

$$[3^{+}\cdot] + 2[\langle 3 \rangle] + [4\cdot] = [4\cdot]_0 \qquad (2)$$

$$[3^{+}\cdot]^2 = K[3^{2+}][\langle 3 \rangle] \qquad (3)$$

$$OD_{1360nm} = \epsilon_{1360}[3^{+}\cdot] \qquad (4)$$

Trials of various absorption coefficients in eq 4 suggested that 1650, the limiting experimental value, was reasonable. K was found to be 4, but other experiments gave rise to a K between ca. 0 and 18. The lowest values were obtained in solutions containing Li$^+$ or Mg^{2+}, implying that 3·· but not 3^{+}· was stabilized by complexation, a conclusion supported by the lack of metal ion effect on the one-electron reduction potential of 3^{2+} and a substantial effect on the two-electron reduction potential.[12] Mohammad et al.[13] have attempted to obtain similar information in work complicated by the use of protic solvents and unknown liquid junction potentials.

The well-defined spectrum for 3^{+}· noted above implies that the spectrum reported by Itoh[6] included a substantial contribution from the cyclomer, *trans*-3.

Conclusions

The sequence shown in eq 5 summarizes the information on the reduction of 3^{2+}. Other polycation systems should provide

$$\langle 3^{2+}\rangle \xrightarrow{e^-} \langle 3^{+}\cdot\rangle \xrightarrow{e^-} \langle 3 \rangle \xrightarrow{M^{n+}} \langle 3\rangle M^{n+} \qquad (5)$$
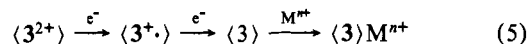
a fertile field for physical organic studies.

Experimental Section

Vacuum line, electrochemical, and thin-film spectroscopic techniques have been described elsewhere.[1] The bispyridinium salts were samples prepared by Dr. Pih-kuei C. Huang, were derived from these samples by ion exchange, or were prepared from trimethylene diiodide and methyl isonicotinate.

(13) Mohammad, M.; Khan, A. Y.f Iqbal, M.; Iqbal, R.; Razzaq, M., *J. Am. Chem. Soc.* **1978**, *100*, 7658–7660.